

Waste and Waste Management

Agricultural Wastes

Characteristics, Types
and Management

Camille N. Foster

Editor

NOVA

WASTE AND WASTE MANAGEMENT

AGRICULTURAL WASTES

CHARACTERISTICS, TYPES AND MANAGEMENT

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CAMILLE N. FOSTER
EDITOR



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CONTENTS

Preface		vii
Chapter 1	Recycling of Agricultural Wastes: Treatment and Uses <i>Z. Ioannou, V. Kavvadias and C. Karasavvidis</i>	1
Chapter 2	Current Utilization of Dairy Industry Co-Products <i>Joshua L. Cohen, Mareen Geissler, Daniela Barile, Christopher W. Simmons and Juliana Maria Leite Nóbrega de Moura Bell</i>	23
Chapter 3	Thermochemical and Biochemical Conversion of Olive Stones <i>Manuel Cuevas, Sebastián Sánchez and Juan Francisco García</i>	61
Chapter 4	Potential Use of Nut Agricultural by-Products in Polymer Materials: A Review <i>Arantzazu Valdés, Ana Beltrán and María Carmen Garrigós</i>	87
Chapter 5	Perspectives on the Utilization of Rice Hull in Productive Processes <i>Mariane Silva de Miranda, Alexandre Correia Lima, Tatiane Faustino de Moraes and Flávio Aparecido Rodrigues</i>	107
Chapter 6	The Use of Agricultural Residues: A Technical and Socioeconomic Challenge for the Biorefinery <i>Araceli García, Cristina Sánchez, Itziar Egüés, Luis Serrano and Jalel Labidi</i>	123
Chapter 7	Valorization of Wastes from Industrial Processing of an Agricultural Product via Thermochemical Conversion Processes <i>Pablo R. Bonelli and Ana L. Cukierman</i>	141
Chapter 8	Agricultural Solid Wastes in Aqueous Phase Dye Adsorption: A Review <i>Sharmeen Afroze, Tushar Kanti Sen and Ming Ang</i>	169
Chapter 9	Coffee Wastes As Adsorbents <i>George Z. Kyzas</i>	215

Chapter 10	Applications of Agricultural Wastes on Bio-hydrogen Production with Bacterial Treatments	231
	<i>Shao-Yi Hsia, Shiuh-Kuang Yang and Huan-Chen Kuo</i>	
Index		251

PREFACE

Agricultural wastes (AW) can be defined as the residues from the growing and processing of raw agricultural products such as fruits, vegetables, meat, poultry, dairy products and crops. Agricultural wastes can be in the form of solid, liquid or slurries depending on the nature of agricultural activities. Furthermore, agricultural industry residues and wastes constitute a significant proportion of worldwide agricultural productivity. Although the quantity of wastes produced by the agricultural sector is significantly low compared to wastes generated by other industries, the pollution potential of agricultural wastes is high on a long-term basis. This book discusses the characteristics, types and management options for agricultural wastes.

Chapter 1 – Agricultural wastes (AW) can be defined as the residues from the growing and first processing of raw agricultural products such as fruits, vegetables, meat, poultry, dairy products and crops. AW can be in the form of solid, liquid or slurries depending on the nature of agricultural activities. Agricultural industry residues and wastes constitute a significant proportion of worldwide agricultural productivity. Although the quantity of wastes produced by the agricultural sector is significantly low compared to wastes generated by other industries, the pollution potential of agricultural wastes is high on a long-term basis. The opportunity and feasibility for recycling these wastes comes from two directions: the care for environment reflected by new sets of rules and regulation and the potential to add value to these wastes by adding positive elements. Moreover, they can be used as precursors in many other sectors such as membranes, biosorbents or activated carbons for the removal of dyes, organic molecules, heavy metals and fertilizers. Different types of agricultural wastes, i.e., deoiled soya, coconut shell, neem leaves, hyacinth roots, rice husk, rice straw, rice bran, lemon leaf, tea waste, potato plants wastes, tomato wastes, sesame hull, garlic peel, peanut hull, carrot stem, carrot leave, barley straw, banana stalk, olive stones, almond shells, peach stones, apricot stones, cherry stones, grape seeds, *Trapa natans* husk, bamboo, doum-palm seed coat, walnut shells, rose seed, pine sawdust and coir pith are ideal raw materials for different industrial applications due to their low cost, non-toxic content and their abundance. The final products derived from agricultural wastes have shown equal or even better properties compared to conventional products concerning separation, adsorption and fertility. Previous studies and projects dedicated to the development of AW treatment technologies focused mainly on the reduction of the wastes organic load and on the reduction or the recovery of valuable substances and succeeded to develop suitable technologies and methods. However, if land distribution is planned the organic load and the toxic substances of treated

wastes should not be the only issues of concern. Specific care should be taken also for inorganic constituents and especially for K, Cl⁻, NO₃⁻, SO₄²⁻, P, Mg, Fe, Zn and others, since the very high concentrations disposed on soil change its quality properties drastically, while electrical conductivity and the concentrations of inorganic soil constituents such as K, P, Fe, Cu remain high even after many years from the last disposal. These practices must take into account important specific local conditions, such as waste characteristic, soil type, background levels of nutrients and pollutants for soil, water and plants, the climate, the relevant crops and the local agricultural practices. Emphasis will be given on specific knowledge and technologies developed so far in Mediterranean countries, their impacts, and constraints and knowledge gaps. Furthermore, policy issues for AW use in Europe and especially in the Mediterranean countries at various levels will be considered. Therefore the aim of this study is to examine the properties and uses of new products derived from agricultural wastes and to research and advance agricultural practices with the use of treated agricultural wastes by recycling nutrients and water from treated agricultural wastes.

Chapter 2 – The design of new food products and agricultural practices have generated a wide diversity of co-products and effluents that often contain a high load of organic matter, from which valuable compounds could be isolated. The surplus and concomitant underutilization of these streams establish serious economic and environmental challenges. Whey, a main co-product arising from cheese manufacturing, was previously considered an environmental pollutant but it is now regarded as a source of many valuable compounds. Among current applications, the production of whey protein concentrates and isolates via ultrafiltration represents the major industrial revenue arising from this stream. The recovery of whey proteins generates an enormous volume of another co-product known as whey permeate. This stream has a high organic load being primarily composed of lactose and minerals. However, recent scientific literature demonstrates the presence of other compounds such as oligosaccharides and peptides, possessing unique bioactivities. Because of the worldwide increase in cheese production, the utilization of whey permeate is under strong scrutiny, with many different strategies being developed to add value to this waste stream. The development of feasible industrial processes to transform, isolate and recover valuable compounds is a key step towards the mitigation of environmental and economic problems arising from constant evolution of our food industry. This chapter focuses on the current utilization and research efforts to valorize whey permeate, where specific processing and environmental challenges are addressed along with the state-of-the-art of the processes and utilizations for the naturally occurring compounds in whey permeate, as well as the valuable products that can be generated from this stream.

Chapter 3 – The olive tree is extensively cultivated in countries of the Mediterranean basin; the area currently under cultivation covers roughly 5.5 10⁶ ha in the EU and 11.0 10⁶ ha in the world. By-products from olive culture and related industries, such as prunings, leaves, olive pomace, and olive stones, are interesting materials for the production of energy, food, fertilizers and other chemicals due to the large available feedstock and their chemical composition. Olive stones are by-products derived from the olive oil extraction industry and from manufacturing of pitted-table olives. Basically, there are two current ways for valorization of olive stones: thermochemical (energy source by combustion, gasification or pyrolysis) and biochemical (ethanol and xylitol production) conversion. Bioconversion of olive stones can also provide other high added-value products such as xylooligosaccharides or

natural antioxidants (tyrosol and hydroxytyrosol). Finally, comparison of the different procedures and potential future applications will be discussed as well.

Chapter 4 – Billion metric tons of agricultural residues are generated every year from industry worldwide that may be considered one of the most abundant, cheap and renewable resources on earth. However, they are normally incinerated or dumped causing environmental problems such as air pollution, soil erosion and decreasing soil biological activity. The reuse of these residues not only prevents environmental concerns, but also can provide farmers the opportunity of a second income from plantation. The incorporation of agricultural residues into polymer matrices is currently a trending topic in research due to the relatively high strength, stiffness and low density of natural fibres present in these residues. Nut by-products, such as almonds (brown hulls, shells and seeds coating) or walnuts (shells), among others, have been used as reinforcement in polymeric materials due to their desirable properties: low density and cost, availability, recyclability, environmental friendliness, total degradation without emission of toxic compounds in composting conditions, and good mechanical properties. On the other hand, nut residues (peanuts, almonds, hazelnuts, chestnuts, walnuts, pecan nuts or pistachios) are rich in bioactive compounds which can be extracted and further used as potential natural additives in food packaging materials with antioxidant and/or antimicrobial activity. In this chapter, different strategies for reusing nut by-products in polymer materials obtaining high value-added materials either as reinforcement or as a source of active compounds are reviewed. Finally, the utilization of gums is currently in the spotlight of the chemical industry.

Chapter 5 – Rice (*Oryza sativa* L.) is a very important component of human diet for many people around the globe. Rice world production is approximately 680 million tons year and Asia leads world harvesting. This is an important source of biomass, especially because there is a tendency to rationalize the use of crude oil and derivatives. Enhancing the utilization of biomass may help to avoid climate and environmental problems. The industrial processing of rice generates some byproducts, such as rice bran and broken rice. Both components can be used as nutritional constituents and they will not be discussed in this work. On the other hand, agricultural residues are relevant in the process, especially rice hull, which accounts for about 20% of the rice crop. This work presents some relevant aspects about the utilization of rice hull. There are many possible applications in different areas, including fermentation and production of ethanol, preparation of cellulose, synthesis of inorganic materials, such as pigments, zeolites, cements, composites, fillers, among others.

Chapter 6 – Biorefining has been defined by the International Energy Agency as the sustainable processing of biomass into a spectrum of marketable products and energy. The concept of sustainability, defined by the World Commission on Environment and Development, arose as consequence, among other reasons, of the energy crisis derived from the imminent depletion of the fossil resources. Thus, a global mindset change is required to face the present scenario, through the reconciliation of three important pillars: economical, societal and environmental issues. Since the current energy system results unsustainable because of imbalance concerns that will have environmental, economical and geopolitical implications far into the future, the sustainable development should be achieved by learning how to use/reuse our resources. In this sense, the use of biomass as a source of products and energy is not new, but its use under a sustainable perspective may imply interesting novelties. With this aim, the Biorefinery outlook should be constructed fulfilling some requirements such as the responsible and optimal exploitation of resources, the application of energy

efficient processes and the accessibility of the resulting energy and products, i.e., a compliance in terms of a viable, bearable and equitable development. The available source of biomass (the biorefinery feedstock) determines not only the range of products obtained in the Biorefinery, but also the more or less specific technology and the optimal conversion pathway required for its transformation. These three parameters (feedstock, technology and conversion pathway) allow classifying the biorefining processes, and their combination offers a huge range of possibilities for the biomass exploitation. The use of agricultural wastes in a biorefinery concept offers a promising perspective of sustainable development. The agricultural activity generates significant quantities of lignocellulosic residues (over 60% of the total crop) that are usually left on the cropland or incinerated to prevent the spread of pests and uncontrolled fires. Against the high availability of this biorefinery feedstock, some other issues appear concerning the use of agricultural residues as bioproducts source: volume variability, crop seasonality, low density, heterogeneous chemical composition, localized generation ... These factors are negatively considered when agricultural wastes are proposed as biorefinery feedstock. In the present work, several crop residues (woody and non-woody wastes) were chemically characterized for determining their contents of the main lignocellulosic components (cellulose, hemicelluloses and lignin). Other biomass components, such as moisture and ash, were also determined. In addition, hot water and weak soda solubilities were measured in order to establish the treatability of these agricultural wastes in a biorefinery concept. According to the results, and after an exhaustive crop production assessment, some biorefinery scenarios were proposed considering different worldwide agricultural productions.

Chapter 7 – Large amounts of wastes arising from industrial processing of agricultural products constitute alternative renewable bioresources potentially attractive for bioenergy generation and/or for the manufacture of other useful products. Their conversion additionally contributes to reduce environmental pollution. The present chapter examines thermochemical conversion of the wastes generated from industrialization of an agricultural product into biofuels and/or products potentially applicable for environmental remediation. The selected wastes arise from industrial processing of whole branches (leaves and twigs) from a native evergreen tree *Ilex paraguariensis*, belonging to the Aquifoliaceae family, for the manufacture of yerba mate. It is a widespread product massively consumed in Southern Latin America countries to prepare a popular herbal tea-like beverage. The commercial final product generally contains less than ~ 35% twigs, since they provide an unpleasantly bitter taste to the infusion, and therefore huge quantities of unused twigs emerge as a by-product. Kinetics for the pyrolysis of the twigs is characterized by non-isothermal thermogravimetric analysis from room temperature up to 900 °C to obtain information for the proper design of full-scale pyrolyzers. A deactivation model which assumes an overall first-order process and considers the physicochemical changes taking place in the biomass with the pyrolysis course through variations of the reaction rate constant with the temperature and solid conversion enables a proper representation of the experimental data over the whole temperature range, with estimated energy activation values between 49 and 137 kJ mol⁻¹. Likewise, yield and characteristics of the three kinds of pyrolysis products, comprising bio-char, bio-oil, and gases, are examined from experiments conducted in a bench-scale fixed-bed installation at temperatures in the range 400 – 700 °C. Gas yield increases with increasing temperature, attaining 43% at 700 °C, while the biochar yield decreases from 30% to 20% with temperature rise. Yield of the bio-oil attains a maximum (53%) at 500 °C, likely arising from

the competition between primary formation of volatiles, at relatively low temperatures, and secondary degradation of the condensable vapors at the higher temperatures. All the pyrolysis products could be used in energy applications. The obtained biochars with higher heating value (HHV) of 23 – 24 MJ kg⁻¹ have potential as environmentally friendly solid biofuel and could be employed for the manufacture of briquettes mainly for domestic use. Accounting for their high stability, as judged from the molar O:C ratio, another possible application could be incorporation of the biochars into the soil for the storage of atmospheric carbon. In turn, the bio-oils show organic fractions with HHV between 28 and 33 MJ kg⁻¹. Density values of the as-produced liquids (~1 kg dm⁻³) are rather higher than those for conventional hydrocarbon fuels due to their higher contents of oxygen and water. The crude bio-oils could be directly burnt or subjected to further upgrading to attain characteristics similar to those of fuel-oil. Pyrolysis of the twigs yields low to medium heating value-gases (5 – 11 MJ m⁻³), mostly composed by CO₂, CO, CH₄ and H₂. Gas composition depends on the temperature, even though CO₂ is the major generated species, followed by CO. Proportion of CO₂ decreases with temperature, particularly at 700 °C, accompanied by enhancements in the HHV of the gaseous mixtures, as a consequence of compositional variations, attaining a maximum value of 11 MJ m⁻³. They might contribute to the energy sustainability of the process. Besides, phosphoric acid activation of the yerba mate twigs at pre-established moderate conditions leads to good quality activated carbons with well-developed porous structures characterized by textural parameters (BET surface area of ~ 1000 m² g⁻¹; total pore volume of 1 cm³ g⁻¹) comparable to those of commercially available samples.

Chapter 8 – Wastewater from many industries such as textile, leather, paper, printing, food, etc. contains large amount of hazardous dyes. Dyes are not biodegradable and photodegradable due to its synthetic origin and complex aromatic nature. Among various physiochemical processes, adsorption techniques are usually widely used to treat dyes laden wastewater. Although commercial activated carbon is the most widely used adsorbent with large success, its use is limited due to high cost and difficulties in regeneration. Therefore there have been explosive growths in research concerning the use of alternative cost effective non-conventional effective adsorbents in the removal of dyes from aqueous solution. In this research direction, agricultural by-product solid wastes which are available in large quantities worldwide with almost through away price are utilized as effective adsorbents in the removal of inorganics and organics from wastewater. The focus of this book chapter is to review extensive literature information about dyes, its classification and toxicity, various treatment methods and finally dye adsorption characteristics by various agricultural by-products solid wastes as adsorbents. The major objective of this chapter is to organize the scattered available information on the adsorptive removal of dyes from its aqueous solution by raw and treated agricultural by-products. Selectively widely used agricultural solid waste adsorbents in the removal of dyes have also been discussed in details here. Finally mechanism, kinetics and adsorptive behaviour of adsorbents under various physicochemical process parameters have been critically analysed and compared. Conclusions have been drawn from the literature reviewed and few suggestions for future research are proposed.

Chapter 9 – One of the most recent trends in environmental technology is the research turn to green chemistry. It is general accepted that one of the most promising techniques for wastewaters treatment is adsorption. In this basis, numerous adsorbent materials have been synthesized up to now. However, there is a novel concept nowadays, which promotes the use of materials with the lowest possible cost. valuation of them for removing of different

pollutants (dyes, cations, anions, etc). In the last years, the instant coffee industry has experienced a constant growth as instant coffee has become one of the most popular kinds of coffee drunk by millions of people around the world. As a consequence, large amounts of coffee grounds, which are the solid residues obtained during the processing of coffee powder with hot water or steam to prepare instant coffee, have been generated worldwide (in the order of 6 millions of tons per year). This work investigates the use of coffee wastes or coffee-based materials as adsorbents for the treatment of wastewaters.

Chapter 10 – At the present time, the demand for energy, goods, and materials is surging because of advanced technology and population growth. However, earth's resources are limited. For this reason, the issues concerning using resources effectively and converting them into energy are important. Taiwan creates a vast amount of agricultural waste every year, which is traditionally burned and buried. The authors do not reuse and recycle agricultural waste, and air pollution is increased when wastes are burned. Therefore, it is necessary to create methods for recycling and reusing agricultural wastes and to transform them into an energy source. This chapter is separated into two parts. The first part will convert agricultural waste into sugar. Agricultural waste is replete with wood fiber that can be reduced into sugar by a microbial method. The second part will use the biological hydrogen production capability of *Clostridium acetobutylicum* ATCC824, with sugar being added to the process. Also, this chapter used ultrasonic treatment for the production of biological hydrogen and calculated the natural frequency of ATCC824. The experiment was designed using the Taguchi method for increasing hydrogen production by using an ultrasonic treatment. Our results showed that the best combination is a temperature of 37 °C, 0.5 MHz ultrasonic frequency, 136 mW/cm² ultrasonic intensity, 10 s exposure time, pH 7.5, and a bacterial concentration of 20%. The outcome of our research can be applied to the production of biomass energy and the research and development of ripening techniques for accelerating fermentable food with biomechatronics.

Chapter 9

COFFEE WASTES AS ADSORBENTS

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ABSTRACT

One of the most recent trends in environmental technology is the research turn to green chemistry. It is general accepted that one of the most promising techniques for wastewaters treatment is adsorption. In this basis, numerous adsorbent materials have been synthesized up to now. However, there is a novel concept nowadays, which promotes the use of materials with the lowest possible cost. valuation of them for removing of different pollutants (dyes, cations, anions, etc). In the last years, the instant coffee industry has experienced a constant growth as instant coffee has become one of the most popular kinds of coffee drunk by millions of people around the world. As a consequence, large amounts of coffee grounds, which are the solid residues obtained during the processing of coffee powder with hot water or steam to prepare instant coffee, have been generated worldwide (in the order of 6 millions of tons per year). This work investigates the use of coffee wastes or coffee-based materials as adsorbents for the treatment of wastewaters.

Keywords: coffee wastes, effluents, adsorption, pollutants

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HISTORY OF COFFEE

Coffee has been consumed for over 1,000 years and today it is the most consumed drink in the world (more than 400 billion cups yearly) [1]. Arabia was responsible for the coffee culture propagation. The most ancient manuscripts mentioning the culture of coffee date from 575 in Yemen, but only in the century XVI in Persia, the first coffee beans were toasted to be turned into the drink that we know today.

Coffee began to be savored in Europe in 1615, brought by travelers. Germans, Frenchmen, and Italians were looking for a way of developing the plantation of coffee in their colonies. But it was the Dutchmen who got the first seedlings and who cultivated them in the stoves of the botanical garden of Amsterdam, a fact that made the drink one of the most consumed in the old continent and becoming a definitive part of the habits of the Europeans. Next, the Frenchmen were given a plant of coffee by the major of Amsterdam, and they began to cultivate in the islands of Sandwich and Bourbon. With the Dutch and French experiences, the coffee cultivation was taken to other European colonies. The European market growth favored the expansion of the plantation of coffee in African countries and was also through the European colonists that coffee reached Puerto Rico, Cuba, Suriname, São Domingos, and Guianas. Through the Guianas, coffee arrived to the north of Brazil. Then, the secret of the Arabs was spread by the entire world.

The coffee tree or shrub belongs to the family Rubiaceae. Coffee beans are produced from the plant *Coffea L.*, of which there are more than 70 species. However, only two of these species are commercially explored worldwide: *Coffea arabica* (Arabica), considered as the noblest of all coffee plants and providing 75% of world's production; and *Coffea canephora* (Robusta), considered to be more acid but more resistant to plagues, and provides 25% of world's production [2, 3]. *C. arabica* is a bush originally from Ethiopia and develops well in high altitudes (600-2,000 m), while *C. canephora* plantations adapt well in altitudes below 600 m.

WASTES IN DURING COFFEE SYNTHESIS

The generation of residues and by-products is inherent in any productive sector. The agro-industrial and the food sectors produce large quantities of waste, both liquid and solid. Coffee is the second largest traded commodity in the world, after petroleum, and therefore, the coffee industry is responsible for the generation of large amount of residues [4]. In the last decade, the use of such wastes has been subject of several studies, but this concern did not exist in past decades (1930 to 1943) when 77 million bags of green coffee were simply burned and released to the sea and in landfills [5]. However, this is an important topic explored nowadays.

In general, "coffee residues" are generally called the solid wastes discarded from the extraction process of instant coffee manufacturing, and the final residues originated from cafeterias. In the last years, the instant coffee industry has experienced a constant growth as instant coffee has become one of the most popular kinds of coffee drink by millions of people around the world. As a consequence, large amounts of coffee grounds, which are the solid

residues obtained during the processing of coffee powder with hot water or steam to prepare instant coffee, have been generated worldwide (6,000,000 t/yr) [6].

Coffee silverskin (CS) and spent coffee grounds (SCG) are the main coffee industry residues. CS is a tegument of coffee beans obtained as a by-product of the roasting process. It is a residue with high concentration of soluble dietary fiber (86% of total dietary fiber) and high antioxidant capacity, probably due to the concentration of phenolic compounds in coffee beans, as well as to the presence of other compounds formed by the Maillard reaction during the roasting process, such as melanoidins [7]. Microscopic examination shows the presence of fibrous tissues from the surface layers of the CS. The main components of these fibrous tissues are cellulose and hemicellulose. Glucose, xylose, galactose, mannose, and arabinose are the monosaccharides present in CS; glucose being found in major amounts. Proteins and extractives are also fractions present in significant amounts in this coffee waste.

SCG is a residue with fine particle size, high humidity (in the range of 80% to 85%), organic load, and acidity, obtained during the treatment of raw coffee powder with hot water or steam for the instant coffee preparation. Almost 50% of the worldwide coffee production is processed for soluble coffee preparation [8]. Therefore, SCG is generated in large amounts, with a worldwide annual generation of 6 million tons [9]. Numerically, 1 ton of green coffee generates about 650 kg of SCG, and about 2 kg of wet SCG are obtained to each 1 kg of soluble coffee produced [10].

ADSORPTION APPLICATIONS

The key-point of each adsorbent material is its adsorption capacity. Three isotherm models are given in recent literature in order to fit the experimental equilibrium data: the Langmuir equation (Eq. (1)) [11], the Freundlich equation (Eq. (2)) [12] and the combinational Langmuir-Freundlich (L-F) equation (Eq. (3)) isotherm model [13]:

$$Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad (1)$$

$$Q_e = K_F C_e^{1/n} \quad (2)$$

$$Q_e = \frac{Q_{\max} K_{LF} (C_e)^{1/b}}{1 + K_{LF} (C_e)^{1/b}} \quad (3)$$

where Q_e (mg/g) is the equilibrium concentration of pollutant in the solid phase; Q_{\max} (mg/g) is the maximum amount of adsorption; K_L (L/mg) is the Langmuir adsorption equilibrium constant; K_F (mg^{1-1/n} L^{1/n}/g) is the Freundlich constant representing the adsorption capacity; n (dimensionless) is the constant depicting the adsorption intensity; K_{LF} (L/mg)^{1/b} is the Langmuir-Freundlich constant; b (dimensionless) is the Langmuir-Freundlich heterogeneity constant.

The amount of total uptake of pollutant in equilibrium (Q_e) was calculated using the mass balance equation (Eq. (4)):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (4)$$

where m (g) is the mass of adsorbent; V (L) the volume of adsorbate; C_0 and C_e (mg/L) are the initial and equilibrium concentrations of pollutant in the liquid phase, respectively.

Recently, many works have been studied for the development of effective and low-cost adsorbents. A published study of Crini [14] reported in details the main low-cost and non-conventional adsorbents for dyes removal (natural materials, biosorbents, waste materials from industry and agriculture). Some of the reported adsorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell) [14-16], industrial waste products (waste carbon slurries, metal hydroxide sludge) [14, 17], biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton) [14, 18]. However, there is a lack of literature dealing with the possible application of coffee residues as adsorbents (i.e for metals, dyes, phenols, etc) [19-24].

Nowicki et al. studied the sorption properties of chars and activated carbons obtained from coffee industry waste materials toward hydrogen sulphide [25]. The effects of pyrolysis temperature and method of activation as well as porous structure, acid-base character of the surface and mineral matter content on the efficiency of H_2S removal are checked. Moreover, four different variants of adsorption test are applied, in order to estimate the optimal conditions of hydrogen sulphide capture. Depending on the method of activation, the adsorbents prepared are characterized by diverse textural parameters, strong basic or medium-acidic character of the surface and various mineral matter content, varying from 1.2 to 58.4 wt%. The results obtained in our study have proved that through an appropriate choice of pyrolysis conditions and activation procedure for coffee industry waste materials it is possible to obtain adsorbents with high capacity of hydrogen sulphide, reaching to 281.5 mg H_2S /gads. The results of our study have also shown that the adsorption ability of activated carbons prepared depends first of all on the conditions of adsorption test, mineral matter content and basicity of the surface and only to a small degree on porous structure development.

The removal of lead by untreated coffee grounds was also investigated in a packed bed up-flow column [26]. The adsorbent used in this study was coffee grounds coming from cafeterias and constitute a waste. It was used with no further treatment just only dried at the ambient air. The experiments were conducted to study the effect of important design parameter such as flow rate (5, 7 and 10 mL/min). Data confirmed that the breakthrough curves were dependent on flow rate. At a bed height of 7.5 cm and flow rate of 10 mL/min, the metal-uptake capacity of coffee grounds for lead was found to be 78.95 mg/g. The breakthrough time increased and the saturation time decreased with the increase of flow rate. The Adams-Bohart, Thomas and BDST models were applied to the adsorption under varying experimental conditions to predict the breakthrough curves and to evaluate the model parameters of the fixed-bed column that are useful for process design. The Adams-Bohart model was in good agreement with the experimental data. The untreated coffee grounds

column study states the value of the excellent adsorption capacity for the removal of Pb (II) from aqueous solution.

Yeung et al. prepared activated charcoal by the pyrolysis of coffee ground waste residues impregnated by phosphoric acid and potassium hydroxide at 600 °C [27]. In our study, spent coffee was collected from the university canteen and the prepared activated charcoal impregnated with potassium hydroxide gave the highest surface area of 708 m²/g, determined by using the methylene blue adsorption method. The activated charcoal was characterized by using scanning electron microscopy and Fourier transform infrared spectroscopy. In order to ensure that the activated charcoal produced is bio-safe, all samples were tested for possible toxic substances, including toxic heavy metals by using ICP-OES, and toxic organics such as acrylamide by using chromatography methods. In addition, all samples showed no ecotoxicity towards *Escherichia coli* and no cytotoxicity toward human HaCaT skin cells. The phosphoric acid activated charcoal demonstrated a high Q_{\max} of 95.2 and 38.2 mg/g, respectively for lead and copper adsorption. For potassium hydroxide activated charcoal, the values of Q_{\max} were found to be 45.4 and 21.2 mg/g, respectively for lead and copper adsorption.

A study of Kumaraswamy presented presents the results of studies carried out on sorption of zinc ions from aqueous solutions by a coffee industry waste s a low-cost sorbent [28]. It was found that crushed coffee industry waste possess relatively high sorption capacity as 46.05 mg/g, when comparing with other sorbents. The biosorption studies were determined as a function of initial metal ion concentrations, pH, biosorbent dosage and biosorbent particle size. About 0.1g of coffee industry waste was found to be enough to remove 71.66% of zinc for 20 mg/L of metal ion concentration from 30 mL aqueous solution. The optimum pH value was found to be 7. The experimental equilibrium data were tested with the biosorption isotherms like Langmuir, Freundlich and their equilibrium parameters were determined. The best-adjusted model to the experimental equilibrium data for coffee industry waste was the Freundlich model.

Another work is concerned with a comparative study to evaluate the adsorptive properties of activated carbons produced from coffee grounds [29]. Activation was done using different chemical activation agents such as H₃PO₄ and ZnCl₂ either separately or mixed together. Characterization of these prepared samples was carried out by determining their physicochemical properties such as specific surface area, porosity, and surface acidity. The results indicated that the produced carbonaceous materials generally developed different and interesting porous structures. Indeed, H₃PO₄-activated carbon (PPAC-P) develops a porous volume of 0.98 cm³/g and a surface acidity of 317.6 meq/100 g (with a high mesoporous proportion). By contrast, ZnCl₂-activated carbon (PPAC-Z) seems to be the most microporous material with a rather limited surface acidity. Adsorption trials with Malathion, a commercial pesticide widely used in Algeria, were carried out onto produced samples of carbonaceous materials in batch experiments at 30°C. Various parameters such as pH, contact time, nature, and amount of adsorbent were investigated for removal efficiency under different operational conditions. Results herein showed that an interesting removal efficiency of 96% was achieved under the following conditions: pH 6, adsorbent amount of 1 g/L, and an equilibrium time of 60 min.

Shen and Gondal used exhausted coffee ground powder (CGP) which proved to be efficient adsorbent for the removal of Rhodamine dyes (i.e., Rhodamine B and Rhodamine 6G) from aqueous solutions by batch adsorption experiments [30]. The morphology, chemical structure as well as the surface property of the as-prepared CGP adsorbent were investigated

by using SEM, FTIR and contact angle meter analytical techniques. The adsorption kinetics and isotherm behaviors of Rhodamine molecules onto CGP were studied and compared using pseudo-1st, pseudo-2nd and Langmuir/Freundlich models, respectively. The maximum adsorption capacities of Rh B and Rh 6G were calculated at 5.255 and 17.369 mmol/g by Langmuir model fitting. The effects of temperature, ionic strength, solution volume and the co-existing anions on the sorption behavior were also investigated. Furthermore, the adsorption mechanism responsible for the efficient removal of dyes is discussed in terms of adsorption process caused by electrostatic and intermolecular forces.

Zuorro and Lavecchia investigated another type of coffee (low-grade coffee beans (LCBs)) as a potential low-cost adsorbent for the removal of methylene blue (MB) from wastewater [31]. The waste was characterized by SEM analysis and FTIR spectroscopy. Equilibrium and kinetic experiments were performed to study the adsorption process. The equilibrium data were found to be well described by the Langmuir model, from which a maximum adsorption capacity of 476.2 mg/g was derived. A half-adsorption time ranging from 12.5 to 96.2 min was estimated by fitting the experimental kinetic data to the pseudo-second-order model.

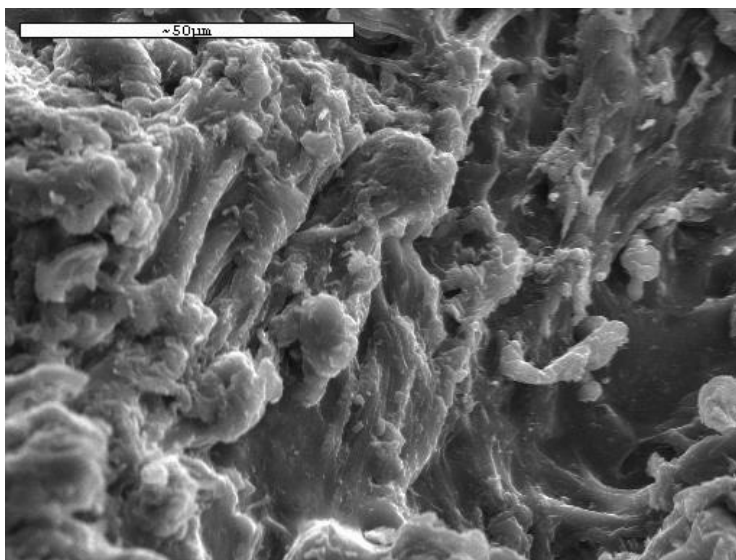


Figure 1. Scanning Electron Micrograph of the untreated coffee residues. Reprinted with permission by Elsevier [33].

Kyzas et al. studied the decolorization of industrial textile wastewaters firstly in batch mode and after the optimization of these conditions, in fixed-bed columns using Greek coffee wastes (COF) as low-cost adsorbents [32]. In this attempt, there is a cost potential given that there was no further modification of COF (just only washed with distilled water to remove dirt and colour, and dried in oven). Also, tests were realized both in synthetic and real textile wastewaters for comparative reasons. The optimum pH of adsorption was acidic (pH 2) for synthetic effluents, while experiments in free pH (non-adjusted) were carried out for real effluents. Equilibrium data were fitted to the Langmuir, Freundlich and Langmuir-Freundlich (L-F) model. The calculated maximum adsorption capacities (Q_{\max}) for total dye (reactive) removal at 25 °C was 241 mg/g (pH 2) and 179 mg/g (pH 10). Kinetic data were fitted to the

pseudo-first, -second and -third order model. The optimum agitation rate and the optimum pH for desorption were determined. The reuse potential showed 10 cycles of adsorption-desorption, in which the reduction in adsorption percentages from the 1st to 10th cycle was 4% for COF adsorbents. Furthermore, experiments dealing the increase of mass of adsorbent showed a strong increase in total dye removal. To direct apply the optimized batch conditions, the same adsorbents were used in fixed-bed columns, performing a complete continuous adsorption/reuse system with low-cost.

A similar study of the above research team used industrial wastes of coffee (untreated coffee residues, UCR) were used as low-cost adsorbents for the removal of dyes (reactive and basic) from single-component aqueous solutions [33]. The cost potential is high given for the non-further treatment of the coffee residues (just only washing with distilled water to remove dirt/color, and drying in oven). The characterization of adsorbents was carried out with SEM micrographs (Figure 1), titrations for point of zero charge (PZC), BET analysis for surface area, titrations (Boehm method) for surface functional groups, and energy dispersive X-ray microanalysis (EDX) for elemental analysis/composition. The optimum pH found after adsorption experiments was pH 2 for reactive and pH 10 for basic dyes. The most interesting of this study is the explanation of the pH-adsorption mechanism. To explain the possible pH-mechanism, the determination of PZC played an important role.

According to PZC, which is determined to be 3.2-3.4, for pH values above of 3.5, a predominant negatively charged surface of UCR is occurred. At lower pH values, the surface charge may get mainly positively charged. In the case of reactive dye (RB), the molecule was instantly dissociated as follows:



Furthermore, the coffee adsorbent was further protonated in acidic pH values (given the already positive charge found from PZC experiments):



As a result, the adsorption process mainly proceeds through electrostatic interaction between the two counterions (UCR^+ and $D-SO_3^-$):



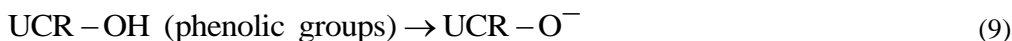
Increasing the pH of the solution ($pH > 3.5$), due to the findings from PZC experiments, the surface of UCR is charged negatively:



However, the RB still remains in negatively charged form ($D-SO_3^-$). So, the interactions decrease, illustrating the reduction of dye (RB) removal. Also, UCR still adsorb dye molecules at intermediate values of pH region (6-8), but in lower percentages (31-22%).

This fact can be explained with a combination of other interactions, as Van der Waals forces and hydrogen bonding [34].

That consideration was strengthened from the surface functional groups of UCR, which are mainly found to be equally carboxylic and basic. In the highly alkaline region (pH 10-12), the strong deprotonation of UCR with simultaneous existence of phenolic groups, in line with the existence of the atom of chloride in the monochlorotriazinyl anchor of dye molecule (functional group) helped to still adsorb in extremely alkaline conditions. The resulting dissociated groups can substitute the chloride atom from the dye molecule in a similar manner as in the dyeing process of textiles, by covalent bonding [34]:



In the case of basic dye (BB), the molecule presented constant positive charge due to the shift of electrons from oxygen to chloride and the already occurrence of amino groups. As described above, the coffee adsorbent was further protonated in acidic pH values (given the already positive charge found from PZC experiments). As a result, the adsorption process is very limited (14%). However, increasing the pH of the solution (pH>3.5), due to the findings from PZC experiments, the surface of UCR is charged negatively. In this way, the deprotonation of the surface of UCR is taken place, transformed to the negatively charged form. So, an interaction between the negative UCR and positive dye begins:



In alkaline conditions, where the full deprotonation dominates, the interaction between adsorbent and dye is completely controlled by electrostatic and coulombic strong forces, between the negatively charged functional groups of UCR (especially the carboxylic groups) and the constant localized positive charge of the cationic dye:



The equilibrium experimental data were fitted to Langmuir, Freundlich, and Langmuir-Freundlich model (best correlation: $R^2 > 0.997$). The calculated maximum adsorption capacities (Q_{max}) for the reactive dye at 25 °C were 179 mg/g (pH 2) and 295 mg/g for the basic one (pH 10) (Figure 2).

Pseudo-first, -second, and -third order kinetic equations were used to fit the kinetic data (pseudo-second order equation presented the most sufficient correlation, $R^2 > 0.992$). Some other adsorption parameters, as agitation rate, initial dye concentration and temperature (25, 45 and 65°C) were also determined.

The desorption was evaluated with experiments for the optimum desorption pH and desorption kinetics, while the ability of reuse was determined with 10 cycles of adsorption-

desorption (the reduction in adsorption percentages from the 1st to 10th cycle was approximately 7% for both dyes). Additionally, experiments in dyeing mixtures were realized in dyeing mixtures composed of (i) separately reactive or basic dyes, and (ii) simultaneously reactive and basic dyes. After the dosage of 3 g/L of adsorbent, a very slight change was observed in equilibrium for all types of dyeing mixtures studied.

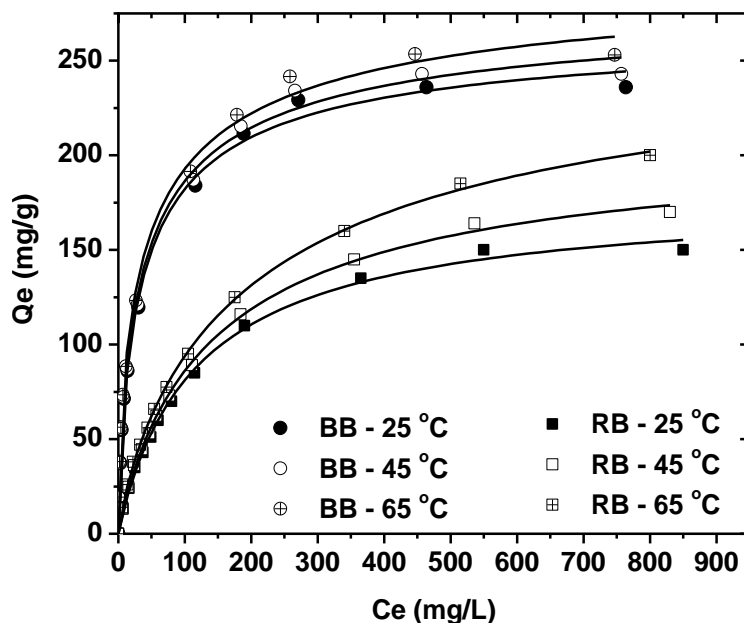


Figure 2. Effect of initial dye concentration and temperature (isotherms) on adsorption of RB and BB onto untreated coffee residues (pH=2, RB; pH=10, BB; 0-1000 mg/L dye concentration; 1 g/L adsorbent; T=25, 45, 65 °C; 140 rpm; 24 h contact). Reprinted with permission by Elsevier [33].

Roh et al. used some waste coffee-grounds (CG) with micro- and macropores as potential biosorbents for the removal of organics or heavy metal ions from aqueous solutions [35]. In several studies, CG was used as adsorbent for removal of heavy metal ions and organics (phenolic compounds). We investigated the potential application of CG as biosorbents for the removal of acid dye (Acid Red 44). To evaluate objectively the adsorption performance of the CG, conventional adsorbent (DA, Degussa alumina) was also tested and our previous reported data for mesoporous materials compared. In adsorption kinetics, experimental data followed the pseudo-second-order kinetic model and intraparticle diffusion was rate-controlled. The maximum uptake (Q_{\max}) capacity of CG proved half of DA, but its adsorption rate was fast (less than 1 h). Namely, Q_{\max} of CG is 27.8 mg/g, and smaller than that of mesoporous adsorbents. However, coffee-ground biosorbent still possesses economical advantages compared to inorganic adsorbents.

Zahoor prepared a type of carbon from Turkish coffee residue and used it to remove crystal violet dye from aqueous solutions [36]. The adsorbent was characterized by surface analyzer, FTIR spectroscopy, Boehm titration and mass titration. Adsorption was studied as a function of pH, dye concentration and contact time. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to describe the kinetic data. The adsorption of

crystal violet dye on prepared adsorbent followed pseudo second order kinetic model rather than pseudo first order kinetic model. The adsorption equilibrium data were analyzed using the Langmuir, Freundlich and Temkin isotherms model. The pH of the solution affects the adsorption capacity of the adsorbent. An increase in the adsorption capacity of the dye was observed with increase in pH. However, this was up to pH 6.5. The increase was insignificant from pH 6.5 to 10. The desorption experiments showed the possibility of regeneration of the adsorbent. Equilibrium was attained within 4 hour for 30 mg/L of dye concentration, while for 25 mg/L and 15 mg/L it was less than 4 h.

Another study studied the use of coffee residues as biosorbents for xenobiotics removal [37]. Spent coffee grounds were magnetically modified by contact with water-based magnetic fluid. This new type of magnetically responsive biocomposite materials can be easily separated by means of commercially available magnetic separators or strong permanent magnets. Magnetic coffee grounds can be used as an inexpensive magnetic adsorbent for the removal of water-soluble dyes. Seven dyes (Crystal violet, Malachite green, Amido black 10B, Congo red, Bismarck brown Y, Acridine orange and Safranin O) were used to study the adsorption process. The dyes adsorption could be described with the Langmuir isotherm. The maximum adsorption capacities reached the value 73.4 mg of dye per g of dried magnetically modified coffee grounds for acridine orange; it corresponds to 276.6 mmol/g. This adsorbent can also be used for magnetic solid-phase extraction of crystal violet from extremely diluted solutions. To conclude, magnetic modification of spent coffee grounds resulted in the formation of a new, promising adsorbent for selected xenobiotics removal.

Another type of study was published by Khenniche et al., in which carbons were prepared from coffee residues using chemical activation with ZnCl_2 [38]. Among five carbons prepared by varying the activating agent ratio (mass of ZnCl_2 /mass of coffee residue) from 0 to 100 %, the one with an activation ratio equal to 25 % (AC 25%) was the most effective sorbent showing the maximum phenol uptake (68%). Consequently, all the adsorption experiments were achieved with the carbon having an activation ratio equal to 25%. A comparative study of prepared activated carbon (AC 25%) and a commercial activated carbon (CAC) was undertaken to determine their capacities for phenol removal. For each adsorbent-phenol system, a pseudo-second order kinetic model described the adsorption kinetics accurately at all concentrations and temperatures for the two systems. The thermodynamics of the phenol-CAC and phenol-AC 25% systems indicate an exothermic process. Phenol adsorption isotherms onto the prepared and commercial activated carbons have been studied. They display two plateaus. The degree of coverage of the surface of two carbons by the phenol molecules was calculated, and it was revealed that the second plateau, appearing at high concentrations, is assigned to the desorption of water molecules fixed on the surface oxygen groups of the activated carbons and the occupation of these sites by phenol molecules in excess in the treated solutions. The Langmuir, Freundlich, and Elovich models were tested.

The same team used coffee wastes as source material to prepare activated carbons by chemical activation with ZnCl_2 [39]. The influence of impregnation ratio (ZnCl_2 /coffee residue) on the physical and chemical properties of prepared carbons is studied in order to optimize this parameter. Texture properties of these carbons were determined by measuring the adsorption of nitrogen at 77 K. The nitrogen adsorption isotherms were interpreted by BET and Dubinin-Radushkevick (D-R) equations. The nature of carbon surface functionalities was studied by Boehm titration method. Phenol and salicylic acid removal from aqueous solutions by adsorption onto the prepared activated carbons was investigated.

The effect of parameters such as pH, agitation time, initial phenol and salicylic acid concentrations, temperature, adsorbent dosage and particle size on phenol and salicylic acid removal were observed. In addition, adsorption kinetics and adsorption isotherms study were realized. Maximum phenol removal was obtained at pH 3 and 20 °C, while for salicylic acid it was obtained at pH 3 and 25 °C. In the isotherm studies, Langmuir and Freundlich isotherm models were applied and it was observed that the phenol experimental data were perfectly described by the Langmuir model while the salicylic acid experimental data were correctly fitted by both Langmuir and Freundlich equations. Batch adsorbent capacity (Q_{\max}) was calculated as 55 mg/g for phenol and 128 mg/g for salicylic acid. The rates of adsorption were found to conform to pseudo-second order kinetics with good correlation.

The potential to remove chromium(VI) from aqueous solutions through biosorption using coffee husk was also investigated [40]. The effects of pH, contact time, initial concentration and adsorbent dosage on the adsorption of Cr(VI) were studied. The data obeyed Langmuir and Freundlich adsorption isotherms. The Langmuir adsorption capacity was found to be 44.95 mg/g. Desorption studies indicated the removal of 60% of the Cr(VI). Infrared spectral studies revealed the presence of functional groups, such as hydroxyl and carboxyl groups, on the surface of the biomass, which facilitates biosorption of Cr(VI).

Boudrahem et al. showed that lignocellulosic materials are good precursors for the production of activated carbon. In this work, coffee residue has been used as raw material in the preparation of powder activated carbon by the method of chemical activation with zinc chloride for the sorption of Pb(II) from dilute aqueous solutions [41]. The influence of impregnation ratio ($\text{ZnCl}_2/\text{coffee residue}$) on the physical and chemical properties of the prepared carbons was studied in order to optimize this parameter. The optimum experimental condition for preparing predominantly microporous activated carbons with high pore surface area ($890 \text{ m}^2/\text{g}$) and micropore volume ($0.772 \text{ cm}^3/\text{g}$) is an impregnation ratio of 100%. The developed activated carbon shows substantial capability to adsorb Pb(II) ions from aqueous solutions and for relative impregnation ratios of 75 and 100%, the maximum uptake is practically the same. Thus, 75% represents the optimal impregnation ratio. Batch experiments were conducted to study the effects of the main parameters such as contact time, initial concentration of Pb(II), solution pH, ionic strength and temperature. The maximum uptake of lead(II) at 25 °C was about 63 mg/g of adsorbent at pH 5.8, initial Pb(II) concentration of 10 mg/L, agitation speed of 200 rpm and ionic strength of 0.005 mol/L. The kinetic data were fitted to the models of pseudo-first order and pseudo-second order, and follow closely the pseudo-second order model. Equilibrium sorption isotherms of Pb(II) were analyzed by the Langmuir, Freundlich and Temkin isotherm models. The Freundlich model gives a better fit than the others. Results from this study suggest that activated carbon produced from coffee residue is an effective adsorbent for the removal of lead from aqueous solutions and that ZnCl_2 is a suitable activating agent for the preparation of high-porosity carbons.

The potential use of spent coffee dusts was also investigated for the removal of Cr(VI) from aqueous solution by Prabhakaran et al. [42]. The removal mechanism was identified as the reduction reaction of Cr(VI) to Cr(III), followed by Cr(III) sorption to the biomass. The phenolic compounds in coffee dusts serve as electron-donor groups for rapid reduction of Cr(VI). The pH edge experiments revealed that Cr(VI) reduction by coffee dusts was independent of pH whereas reduced Cr(III) adsorption onto biomass was strongly dependent on pH. Isotherm experiments revealed that coffee dusts possess maximum chromium uptakes of 39.0 mg/g (pH 4). Among the two isotherm models (Langmuir and Toth), the Toth model

better described the chromium biosorption isotherms with high correlation coefficients and low percent error values. A kinetic model based on the redox reaction between Cr(VI) and biomass successfully described the kinetic data.

Oliveira et al. proposes an alternative use for coffee husks (CH), a coffee processing residue, as untreated sorbents for the removal of heavy metal ions from aqueous solutions [43]. Biosorption studies were conducted in a batch system as a function of contact time, initial metal ion concentration, biosorbent concentration and pH of the solution. A contact time of 72 h assured attainment of equilibrium for Cu(II), Cd(II) and Zn(II). The sorption efficiency after equilibrium was higher for Cu(II) (89-98% adsorption), followed by Cd(II) (65-85%) and Zn(II) (48-79%). Even though equilibrium was not attained in the case of Cr(VI) ions, sorption efficiency ranged from 79 to 86%. Sorption performance improved as metal ions concentrations were lowered. The experimental sorption equilibrium data were fitted by both Langmuir and Freundlich sorption models, with Langmuir providing the best fit ($R^2 > 0.95$). The biosorption kinetics was determined by fitting first and second-order kinetic models to the experimental data, being better described by the pseudo-second-order model ($R^2 > 0.99$). The amount of metal ions sorbed increased with the biosorbent concentration in the case of Cu(II) and Cr(VI) and did not present significant variations for the other metal ions. The effect of the initial pH in the biosorption efficiency was verified in the pH range of 4-7, and the results showed that the highest adsorption capacity occurred at distinct pH values for each metal ion. A comparison of the maximum sorption capacity of several untreated biomaterial-based residues showed that coffee husks are suitable candidates for use as biosorbents in the removal of heavy metals from aqueous solutions.

Kaikake et al. studied the feasibility of using coffee beans after being dripped and degreased (DCB) as an adsorbent for base metals such as Cu(II), Zn(II), Pb(II), Fe(III) and Cd(II) were examined [44]. The plant cell wall in DCB has the porous structure from the scanning electron microscopy (SEM) analysis, and the specific surface area was determined to be $1.2 \text{ m}^2/\text{g}$ using the specific surface area analyzer. Batch adsorption experiments on DCB were carried out at various pHs in order to elucidate the selectivity of metal ions. All metals were adsorbed at low pH region (3.0-5.0). Of particular interest was the adsorption characteristics of Cd(II) on DCB. The adsorption isotherm for Cd(II) at pH 8 fitted with a Langmuir equation to yield an adsorption equilibrium constant of $55.2 \text{ mmol}/\text{dm}^3$ and an adsorption capacity of $5.98 \times 10^{-2} \text{ mmol}/\text{g}$. The desorption of Cd(II) was easily achieved over 90% by a single batchwise treatment with an aqueous solution of hydrochloric acid or nitric acid at more than 0.01 mol dm^{-3} . These results suggested that DCB behaves as a cation exchanger.

The adsorption behavior of heavy metals on arabica and robusta roasted coffee beans was investigated by Minamisawa et al. [45]. To adsorb heavy metals, the coffee beans residues were suspended in aqueous solutions containing Cu(II) or Cd(II). Then the amount of heavy metal remaining in the solution was measured by atomic absorption spectrometry. The results show that the adsorption percentage of the heavy metal ions were above 90% for all coffee beans examined. Further, the adsorption capacities of Cu(II) and Cd(II) ions onto blend coffee were about $2.0 \text{ mg}/\text{g}$. This adsorption capacity is similar to that of zeolite, activated carbon and chitosan; and is higher than that of chitin and cerite. Blend coffee was thus found to be a good adsorbent for the removal of heavy metals from wastewater.

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